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In situ DRIFT study of dimethyl ether carbonylation to methyl acetate on H-mordenite

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ABSTRACT

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to study the reaction of dimethyl ether (DME) carbonylation to methyl acetate (MAc). Methoxyl and acetyl groups were observed in situ, confirming the reaction mechanistic proposal. DME adsorption bands on Si—OH, Al—OH and SiOHAl (Brønsted acid sites) groups were identified respectively. The effect of temperature and pressure on acetyl formation and side reactions were systematically studied. It was found that methoxyls formed by DME chemisorbed on Brønsted acid sites could be observed above 433 K. High pressure and appropriate temperature interval promoted the formation of acetyls. Side reactions, DME transformed into olefins and then into cokes, were favored at low pressure and high temperature. Carbonylation reactions on catalysts with acid sites only in 8MR side pockets and 12MR main channels of mordenite (samples noted as HMOR-SP and HMOR-MC) were conducted by in situ DRIFT spectroscopy and catalytic testing. Pyridine molecules adsorbed in 12MR main channels resulted in the low utilization of acid sites in 8MR side pockets. The synthesis rate of MAc on HMOR-SP was stable but lower. HMOR-MC presented the lowest MAc synthesis rate with the production of coke, which was also observed in DRIFT spectra.

1. Introduction

Ethanol, one of the most important renewable fuels, can be used as fuel additive, hydrogen carrier, chemical feedstock, and so on. The production and transformation of ethanol have been triggering wide research interest [1–4]. Traditional commercialized route by hydration of ethylene to ethanol employs non-renewable oil as raw material, whereas limited production capacity of ethanol by fermentation of biomass materials cannot meet large-scale demands in various fields [3]. The synthesis of ethanol by DME carbonylation to MAc and MAc hydrogenation is a potential way from synthesis gas ($CO + H_2$, syngas) which can be derived readily from natural gas, coal and biomass [5,6].

Porous materials are important in widespread processes such as catalysis, molecular separations, energy and health, in which porous zeolites have made the largest contribution to society so far, and the field is still developing rapidly [7,8]. The synthesis of porous materials by templates have been well reviewed in literature [9]. Researches on DME carbonylation by heterogeneous catalysts have been gaining much attention and great progress have been made on the active sites [10–12], the stability of catalysts [13] and the positive enhancement of metal atoms [14–16] since Fujimoto first reported that HMOR was effective for the catalysis of DME to MAc in 1984 [17].

The intermediates and elementary steps of DME carbonylation reaction on zeolites have been proposed by Iglesia et al. [10,18,19]. They suggested that DME first adsorbed on the Brønsted acid sites of zeolite to form methanol and a chemisorbed methyl group CH_3^* at zeolite exchange sites, and then CO inserted the C-O between the chemisorbed methyl group CH_3^* and the oxygen atom of zeolite framework to produce CH_3CO^*. This crucial intermediate CH_3CO^* reacted with another DME molecule to form MAc and the surface methyl group was regenerated. Therefore, the direct observation of CH_3^* and CH_3CO^* under real reaction conditions would be prerequisite to confirm this mechanism proposal.

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Cheung et al. had tried to prove this mechanism by infrared spectroscopy. They observed the surface acetyl CH_3CO^* by dissociative adsorption of acetic anhydride on HMOR zeolite at 438 K [19]. So, the acetyl came from the reaction of material containing carbonyl group and the O-H of zeolite, not from the reaction of DME and CO under the real carbonylation reaction conditions. In addition as described in article, acetic anhydride could only react with Brønsted acid sites in twelve-member ring (12MR) main channels but not access those in side-pockets of mordenite, which were considered as the real active centers of DME carbonylation reaction [10,11]. Andrzej Malek reported the observation of acetyl group in order to explore the source of the first C-C species in MTO reaction [20]. The systematic study about the mechanism of DME carbonylation reaction, especially the observation and the variation of intermediates, methoxyl and acetyl, under real DME carbonylation reaction conditions, would help us to understand the reaction in depth.

In order to relate the reaction products and the adsorbed species, in situ information is essential. In this sense, in situ DRIFT spectroscopy can be regarded as an ideal technique. DRIFT spectroscopy is an increasingly popular technique in catalysis research since Kőrtűum and Griffiths proved its fundamental principle theoretically in 1970s. This technique has been widely used to characterize the catalyst and surface species prior to and under reaction conditions and thus can provide vital information about reactions. Moreover, it permits in-situ observation of the reactor bed in powdered or granular form without any catalyst manipulation, not in wafer with the negative effect of the diffusion of reactants and products. Therefore, DRIFT spectroscopy is an invaluable method for studying powders, rough-surfaced solids and the reactions on powders, which is close to the actual state of the true reactions [21,22], and this method has been successfully used to study the mechanism of many reactions, such as the low-temperature methanol synthesis mechanism using ethanol promoter [23], the selective catalytic reduction of NO_x with NH_3 [24–26], the ethanol steam-reforming reaction [27], water-gas shift reaction [28] and CO oxidation at room temperature on Au/SiO_2 [29]. In this study, we used in situ DRIFT spectroscopy to study DME carbonylation reaction and observed the intermediates of methoxyl and acetyl groups on HMOR by DME reacting with CO under the real reaction conditions. Systematic study was carried out about DME adsorption on the HMOR, the effect of temperature and pressure on the acetyl formation and side reactions and the distinct effect of acid sites at different channels of HMOR on DME carbonylation reaction.

2. Experiment

2.1. Catalysts preparation

The materials, synthesis processes and characterization results of HMOR were presented elsewhere [15]. The sample marked as HMOR-MC (with acid sites only in 12MR main channels and the counter ions in 8MR side pockets were Na^+) was obtained by the ion exchange of NaMOR with NH_4NO_3 aqueous solution (0.1 mol L^{-1}, 1 g of the solid in 10 mL of the solution) at room temperature for 0.5 h. After filtered and washed with deionized water, the solid was dried and calcined in flowing dry air. Na content left in HMOR-MC was 2.5 wt% analyzed by XRF, about 53% of the total Na content in NaMOR 4.7 wt%. HMOR-SP (with acid sites in 8MR side pockets only) was prepared by adsorption of pyridine molecules to neutralize the acid sites in 12MR main channels of HMOR [13,30].

2.2. In situ DRIFT spectroscopy study

In situ DRIFT spectra were collected on a Bruke Tensor 27 instrument supplied with a diffuse reflectance attachment and with a MCT detector. The catalyst powder was contained in the diffuse reflectance infrared cell with ZnSe window which could work at high temperatures and high pressures. In situ absorbance spectra were obtained by collecting 16 scans at 4 cm^{-1} resolution.

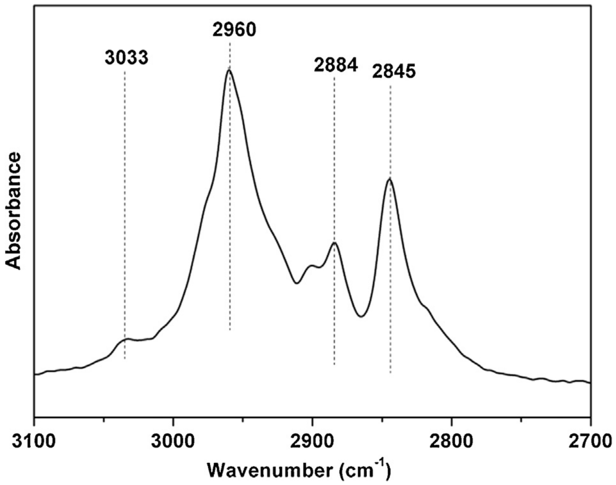

Fig. 1. In situ DRIFT spectrum of DME on γ-Al_2O_3 at 403 K.

DME used in experiments was 3% in volume and N_2 was the equilibrium gas. The degree of purity of CO and purging N_2 was 99.999%, respectively.

Before the adsorption of reactants, the sample was first calcined in situ in N_2 stream flowing 30 cm^3 min^{-1} at 723 K (523 K for HMOR-SP) for 120 min. Subsequently the catalyst was cooled down to adsorption temperature in N_2 stream, and the spectrum of catalyst was recorded as reference.

The spectra could be obtained continuously during the adsorption and reaction processes thus we could study the variation of surface intermediates over time. The spectra were obtained according to the following procedure after the catalyst pretreatment: the activated catalyst was exposed to DME at a total rate of 10 cm^3 min^{-1} at reaction temperature for 5 min, followed by sweeping in N_2 for 30 min to yield the adsorbed DME species on catalyst surface. As gaseous CO did not have effect on the observation and intensity of acetyl bands, so the spectra of acetyl were obtained continuously as CO passed through the in situ cell at different temperatures and pressures. Then DME was carried into the cell again. Gaseous products were observed by online mass spectrometer (Omnistar).

3. Results and discussion

3.1. Adsorption of DME on aluminum hydroxyls, silanols and Brønsted acid sites

In situ DRIFT spectra of DME adsorption on aluminum hydroxyl (AlOH), silanol (SiOH) and HMOR are shown in Figs. 1–4 . The adsorptions of DME on AlOH and SiOH were conducted on γ-Al_2O_3 and SiO_2, mainly with the AlOH and SiOH at 3660 and 3740 cm^{-1}, respectively. There are four bands, 3033, 2960, 2884 and 2845 cm^{-1}, in the spectrum of DME adsorption on AlOH in Fig. 1. Assignment of the bands was made by analogy with the spectrum of known compounds and by comparison with published literatures. The bands at 3033 and 2960 cm^{-1} were the two asymmetric stretching modes of CH_3, respectively. The band at 2845 cm^{-1} was the symmetric stretching mode of CH_3. The 2884 cm^{-1} was assigned to the overtone of the deformation mode of CH_3. Those bands indicated the formation of methoxyl groups of DME adsorption on AlOH at 403 K [31].